



Syngas production by carbon dioxide reforming of methane over different semi-cokes

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H I G H L I G H T S

- CH₄–CO₂ reforming over different semi-cokes has been studied.
- With the catalytic activity varying with different types of semi-cokes.
- The lower the coal rank, the more surfaces and pore, the better catalytic activity.
- Function groups of semi-cokes are participated in the CH₄–CO₂ reforming.

A R T I C L E I N F O

Article history:

Received 14 October 2012

Received in revised form

14 December 2012

Accepted 1 January 2013

Available online 9 January 2013

Keywords:

Semi-cokes

Carbon dioxide reforming of methane

Catalyst

Syngas

A B S T R A C T

Carbon dioxide reforming of methane over different semi-cokes (Hongce lignite, Shenmu bituminous coal and Jincheng anthracite) is being investigated at atmospheric pressure, temperature of 800–1000 °C, CH₄/CO₂ ratios of 3:1–1:3 and gas–solid contact times of 0.11–1.76 min using a fixed-bed reactor. The semi-cokes still shows stable catalyst activity after 480 min of reaction. The results show that the catalyst activity of the semi-cokes was lower with increasing coal rank. The order of the catalyst activity is Hongce lignite semi-cokes > Shenmu bituminous coal semi-cokes > Jincheng anthracite semi-cokes. This is somewhat related to the content of the functional groups of the semi-cokes. The analysis for the surface structure of the semi-cokes before and after the reforming reaction shows that the C=O and –NH₂, etc., functional groups on the surface of the semi-cokes participated in the reforming reaction, the coal rank and the BET are the main factors which influenced the catalyst performance, and the functional groups on the surface of the semi-cokes and the types and amounts of alkaline metals have a certain type of influence on the activity of the reforming reaction.

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1. Introduction

Carbon dioxide reforming of methane can reduce the harm generated from greenhouse gas, and it can generate a resource gas for the Fischer Tropsch synthesis [1,2], so it has been widely investigated. Currently, studies on the catalysts used in CH₄–CO₂ reforming are mainly focused on the noble metals and transition metals used [3–7]. However, the noble metals are expensive and these resources are limited. And the transition metals are easily deactivated due to carbon deposition, so it has become the bottleneck of its industrial application.

Semi-cokes are the product of coal after low-temperature (450–750 °C) dry distillation, and the main ingredients in semi-cokes are carbon, ash and volatile compounds. There are many types of

mineral substances and abundant functional groups in semi-cokes. Semi-cokes are porous materials and the composition, BET, volume and average pore diameter of semi-cokes are different with different coal rank and pyrolysis temperature. The BET surface area is higher than raw coal and its reaction activity is strong. Although the BET of semi-cokes is lower than that of activated carbon, its mechanical strength is higher [8]. It can be used as the catalyst or as the carrier for a catalyst, and the feasibility of the reaction and the catalytic function of semi-cokes have been demonstrated during hydrogen cracking [9–13]. Currently, researchers have performed preliminary studies on the catalytic function of semi-cokes in CH₄–CO₂ reforming [14–18], but the studies have not been highly systematic and a deepening of the understanding of the mechanism of the interactive function of the semi-cokes and reaction gas is still required.

This article investigates the effects of Hongce lignite (HC), Shenmu bituminous coal (SM) and Jincheng anthracite (JC) on the CH₄–CO₂

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Table 1
Proximate and ultimate analysis of semi-cokes.

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
	Moisture	Ashes	Volatiles	Fixed carbon	C	H	O	N	S
HC	4.95	13.57	14.02	67.46	73.68	6.24	18.05	1.55	0.48
SM	2.16	11.20	13.34	73.3	84.88	5.26	7.56	1.82	0.48
JC	3.21	11.33	4.98	80.48	95.50	1.39	1.81	1.14	0.16

reforming by using a fixed-bed reactor. The factors affecting the catalyst stability and activity, such as the reaction temperature, the gas–solid contact time, the ratio of CH_4/CO_2 and the coal rank were investigated, and the changes of the surface properties of the semi-cokes before and after the reaction were also investigated.

2. Experimental

CH_4 – CO_2 reforming was carried out in a horizontal corundum tube reactor (20 mm inner diameter, 100 cm in length), and 10.0 g of the catalyst was placed in the middle of the corundum tube reactor, which was filled with broken tiles on both ends to guarantee that the catalyst was in the constant temperature area of the reactor. The flows of CH_4 and CO_2 were individually controlled by two mass flow meters (the range of flow control was 0–200 ml min^{-1}), and the reaction temperature was in the range of 800–1000 °C and heating rate 20 °C min^{-1} . The flow of generated gas was measured by a soap foam flow meters, the gas composition and content were measured by gas chromatography (GC-950 to measure CO_2 , CH_4 and CO and GC-9890 to measure H_2). Table 1

presents the data proximate and ultimate analysis of the semi-cokes before and after the reforming reaction.

From the proximate analysis, it can be observed that the Hongce lignite semi-cokes have high ash content but low fixed carbon content. The volatilising content of both the Hongce lignite semi-cokes and the Shenmu bituminous coal semi-cokes are high. The fixed carbon content of the Jincheng anthracite semi-cokes is the highest, but the ash content and volatilising content are lowest. The ultimate analysis shows that the oxygen content of the Hongce lignite semi-cokes is the highest at 18.05%, and the oxygen content of the Shenmu semi-coke is 7.65%. For the Jincheng semi-cokes, the coal rank is highest, the proportion of carbon content is largest and the oxygen content is lowest. The amount of oxygen determines the amount of oxygen functional groups that the semi-cokes contain.

3. Results and discussion

3.1. Effect of coal rank

The semi-cokes used in the laboratory had diameters of 3–5 mm, a weight of 10.0 g and a length of approximately 10 cm in the corundum tube. Fig. 1 shows the conversions of methane (a) and carbon dioxide (b) and the yields of carbon monoxide (c) and hydrogen (d) from the CH_4 – CO_2 reforming over different semi-cokes under the following conditions: normal atmospheric pressure, CH_4/CO_2 ratio of 1:1, total flow of 36 ml min^{-1} and temperature of 900 °C.

It can be observed from Fig. 1(a) and (b) that the maximum conversion rates of CH_4 and CO_2 are 2.8% and 1.9% without catalyst,

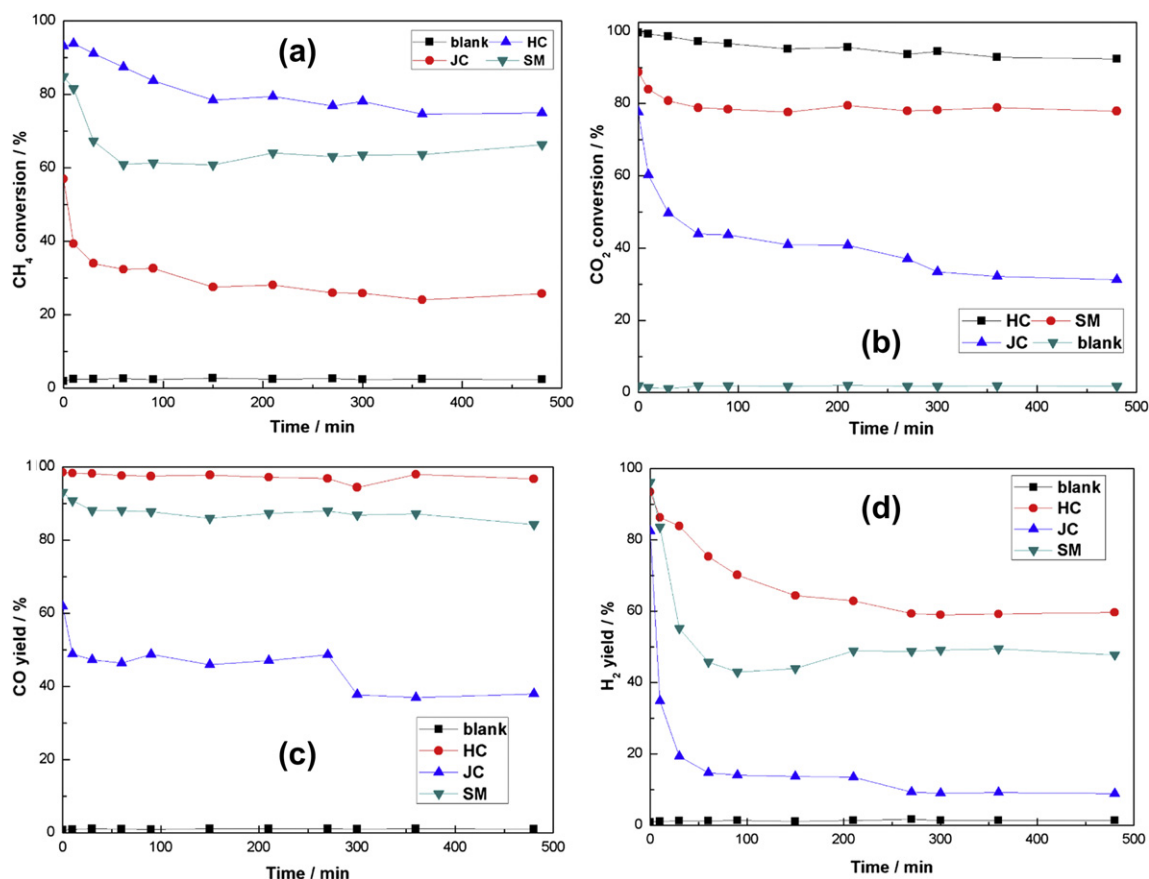


Fig. 1. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c) and hydrogen yield (d) versus time over different semi-cokes.

respectively, so it can be concluded that the impact of the CH₄–CO₂ reforming without catalyst can be considered negligible.

We can also see from Fig. 1(a) and (b) that the conversion rates of CH₄ and CO₂ showed the same trend under the catalysis by different semi-cokes, that is, the initial conversions were all initially high, slowed down gradually as the reaction time increased, and then were stable after 50 min. Fig. 1(c) and (d) shows that the trend in the yields of CO and H₂ was basically the same as the trend in the conversions of CH₄ and CO₂. This is because the carbon deposition generated from the cracking of CH₄ covered the active sites on the surface of the semi-cokes, which can lower the activity of the semi-cokes, but the gasification of CO₂ and the deposited carbon partially eliminated the carbon deposition on the surface of the semi-cokes, which can increase the active sites of the semi-cokes. The conversions of CH₄ and CO₂ tend to be stable when the rate of carbon deposition and gasification are in balance.

It is clearly observed from Fig. 1 that when the reaction became stable, the order of the catalyst activity was Hongce lignite semi-cokes > Shenmu bituminous coal semi-cokes > Jincheng anthracite semi-cokes. This is related to the size of the respective BET of the semi-cokes. In addition, the BET of the Hongce lignite semi-cokes was basically the same as that of the Shenmu bituminous coal semi-cokes, but the catalytic effect was much stronger, indicating that the BET was not the only factor that influenced the catalytic performance. Mariana de et al. [19] showed that the activity of the catalyst is related to the functional groups and the types and amounts of alkaline metal oxides the catalyst contains. Considering the above factors comprehensively, the Hongce lignite semi-cokes have better catalytic activity.

3.2. Effect of temperature

Fig. 2 displays the conversions of methane (a) and carbon dioxide (b) and the yields of carbon monoxide (c) and hydrogen (d) of the CH₄–CO₂ reforming at different reaction temperatures under the following conditions: normal atmospheric pressure, 10.0 g of semi-coke, CH₄/CO₂ ratio of 1:1, total flow of 36 ml min^{−1} and temperature of 800–1000 °C.

From Fig. 2(a) and (b), it can be observed that the CH₄ and CO₂ conversions showed the same trend over time for the different semi-cokes, that is, the conversion increased as the temperature increased. When the Hongce lignite semi-cokes were used as the catalyst and the temperature was raised from 800 °C to 1000 °C, the CH₄ and CO₂ conversions increased from 62.5% and 83.9% to 93.1% and 99.7%, respectively. The CH₄–CO₂ reforming is a strongly endothermic reaction, so increasing the reaction temperature had a positive effect on the reforming reaction. By comparing Fig. 2(a) and (b), it can be observed that the CO₂ conversion was higher than that of CH₄ at the same temperature, which implies that the gasification reaction for CO₂ and carbon is taking place during the reforming process $C + CO_2 = 2CO$ ($\Delta H = +159.7 \text{ kJ mol}^{-1}$).

It can be observed from Fig. 2(c) and (d) that the CO and H₂ yields increased as the reaction temperature increased. However, the CO yield was higher than that of H₂ because as the temperature increased, the gasification function of CO₂ intensified and the amount of CO generated was much higher. Additionally, as the temperature increased, a small amount of water was generated, and the increase in the temperature was favourable for the reaction of $CO_2 + H_2 = CO + H_2O$ ($\Delta H = +41.1 \text{ kJ mol}^{-1}$), promoting the generation of water, which lowered the yield of hydrogen.

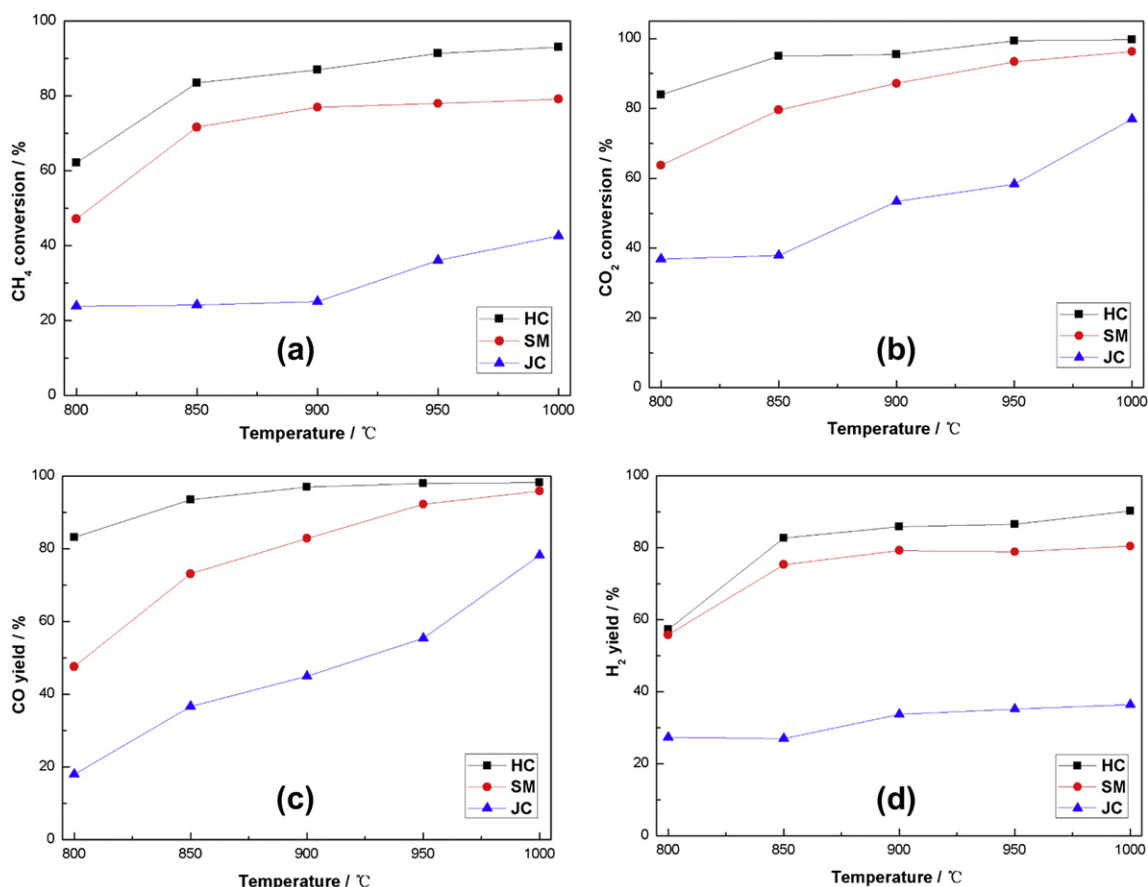


Fig. 2. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c) and hydrogen yield (d) versus temperature over different semi-cokes.

From the effects of temperature on the conversion and yield, it can be concluded that increasing the temperature improves the conversion of the reaction gas and the generation of the syngas, however, increasing the temperature will also increase the energy consumption. Additionally, as the temperature increases, the gains in conversion and yield are not significant when it reaches the heat balancing state, so an adequate reaction temperature is required. An adequate reaction temperature can not only reduce the energy consumption but also enable higher conversions of CH_4 and CO_2 . Under the tested conditions, the adequate temperature was 900°C .

3.3. Effect of the gas–solid contact time

Fig. 3 displays the conversions of methane (a) and carbon dioxide (b) and the yields of carbon monoxide (c) and hydrogen (d) of the CH_4 – CO_2 reforming at different gas–solid contact times under the following conditions: normal atmospheric pressure, 10.0 g of semi-coke, CH_4/CO_2 ratio of 1:1, total flow of $18\text{--}288\text{ ml min}^{-1}$ and temperature of 900°C .

From Fig. 3(a) and (b) it can be observed that the conversions of CH_4 and CO_2 over different semi-cokes increased as the gas–solid contact time increased. When the gas–solid contact time increased from 0.11 min to 0.87 min, the conversions of CH_4 and CO_2 showed a linear increasing trend as the gas–solid contact time increased. However, when the gas–solid contact time was longer than 0.87 min, the conversions of CH_4 and CO_2 did not change much as the gas–solid contact time continually. When the gas–solid contact time was short, the amount of contact between the reaction gas and the activity sites on the semi-cokes was

reduced and a portion of the reaction gas flowed out with the syngas because it had no time to react, which resulted in the decreased conversion rates. When the gas–solid contact time was increased, the reaction gas and the activity sites of the semi-cokes had enough time to react and the reaction gas could diffuse deeply into the interior pores of the semi-cokes and react with more activity sites, thus raising the conversions of CH_4 and CO_2 . When the gas–solid contact time reached a certain level, the contact between the reaction gas and the activity sites of the semi-cokes reached a saturated state, under this condition, continually increasing the gas–solid contact time did not enhance the conversions of CH_4 and CO_2 .

It can be observed from Fig. 3(c) and (d) that the effect of the gas–solid contact time on the yields of CO and hydrogen was basically the same as the effect on the conversions of CH_4 and CO_2 . Considering the Hongce lignite semi-cokes as an example, when the gas–solid contact time was 0.87 min, the yield of hydrogen and CO was 86.56% and 95.93%, respectively. When the gas–solid contact time was increased to 1.74 min, the yield of hydrogen only increased in 0.79 percentage points to 87.35% and the yield of CO only increased in 0.25 percentage points to 96.22%. Therefore, when the gas–solid contact time is above 0.87 min, increasing the gas–solid contact time to enhance the yields of hydrogen and CO is not very ideal.

3.4. Effect of the CH_4/CO_2 ratio

Fig. 4 displays the conversions of methane (a) and carbon dioxide (b) and the ratio of H_2/CO (c) for the CH_4 – CO_2 reforming at

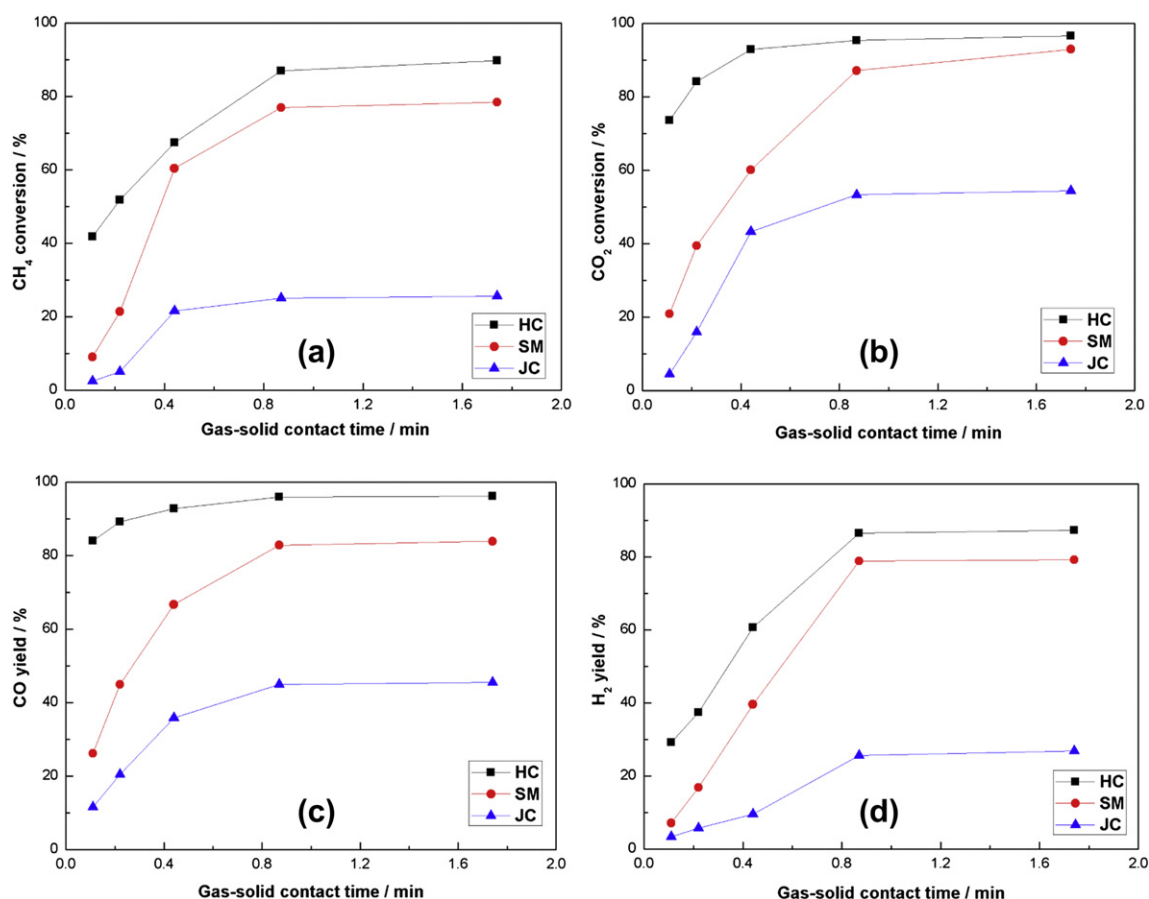


Fig. 3. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c) and hydrogen yield (d) versus gas–solid contact time over different semi-cokes.

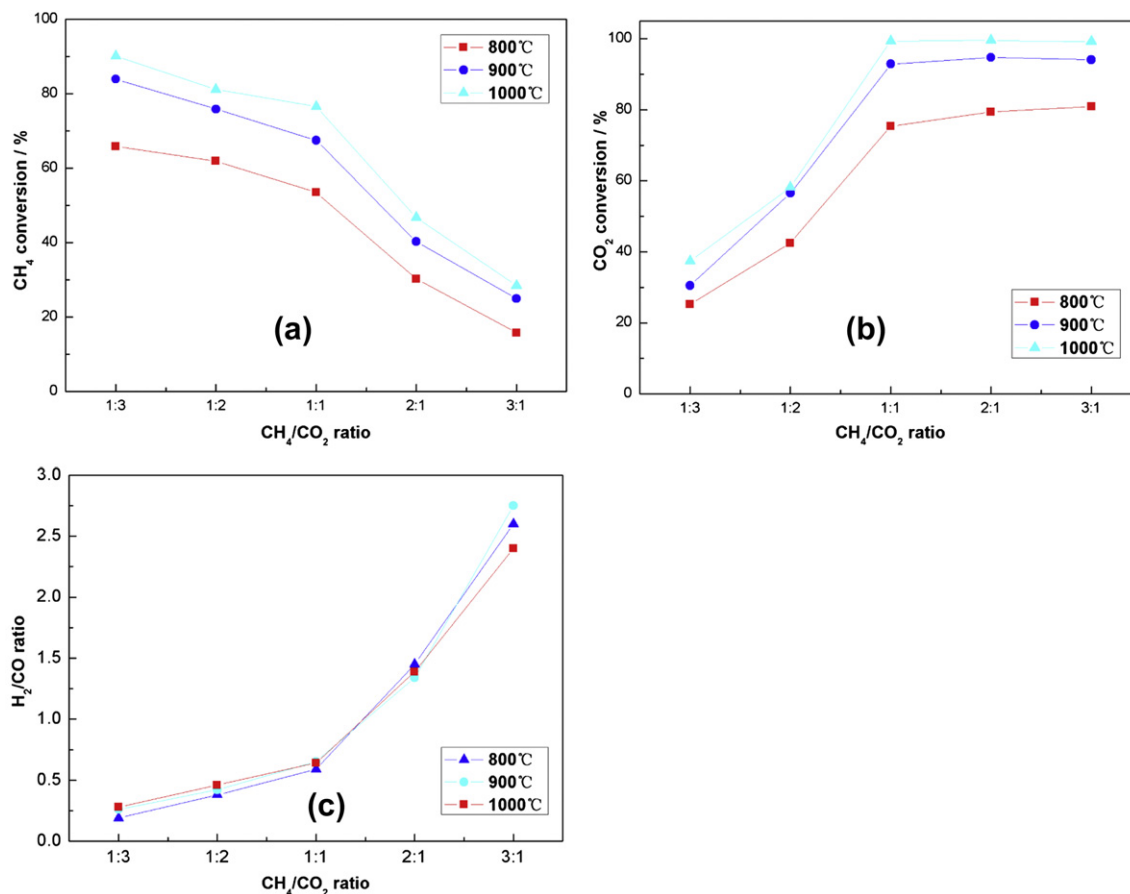


Fig. 4. Methane conversion (a), carbon dioxide conversion (b) and H_2/CO ratio (c) versus the ratio of CH_4/CO_2 .

different ratios of CH_4/CO_2 under the following conditions: normal atmospheric pressure, 10.0 g of semi-coke, CH_4/CO_2 ratios of 1:3–3:1, total flow of 72 ml min^{-1} and temperature of 800–1000 °C.

From Fig. 4(a) and (b), it can be observed that as the ratio of CH_4/CO_2 increased, the conversion of CH_4 showed a gradually decreasing trend and the conversion of CO_2 showed a monotonously increasing trend at different reaction temperatures. While from the point of view of reaction balancing, the CO_2 conversion should increase the concentration of CH_4 , there are also CH_4 cracking and CO_2 gasification reactions taking place during the reforming reaction. Due to the CH_4 cracking reaction, the carbon deposition increased as the CH_4 concentration of the reaction gas increased, and the carbon deposited on the surface of the semi-coke catalyst blocked the micropore and reduced the chances for the reaction gas

of hydrogen in the syngas, and increasing the concentration of CO_2 increases the amount of CO in the syngas. Under the tested conditions, the ratio of H_2/CO was 0.19–2.75, and the ratio of H_2/CO in the syngas can be adjusted by changing the ratio of CH_4/CO_2 to meet different chemical synthesis needs.

3.5. Carbon balance

Fig. 5 displays the carbon balance value of the $\text{CH}_4\text{--CO}_2$ reforming at different reaction temperatures under the following conditions: normal atmospheric pressure, 10.0 g of semi-coke, CH_4/CO_2 ratios of 1:1, total flow of 72 ml min^{-1} , reaction time 72 h and temperature of 800–1000 °C. The formula of carbon balance value was as follows:

$$\text{Carbon balance value} = \frac{\text{C content of CH}_4, \text{CO}_2 \text{ and CO in production gas}}{\text{C content of CH}_4 \text{ and CO}_2 \text{ in feed gas}}$$

and catalyst to come into contact, and, in this way, lowered the catalytic activity of the semi-coke.

It can be observed from Fig. 4(c) that the ratio of H_2/CO increased as the ratio of CH_4/CO_2 increased, but comparatively, the effect of the reaction temperature on the ratio of H_2/CO was not obvious. Increasing the concentration of CH_4 increases the amount

It can be observed from Fig. 5, carbon balance value increased with the reaction temperature and more than 1 above 900 °C. It indicates that carbon content of the production gas is more than that of the feed gas. The three main reactions which may occur in $\text{CH}_4\text{--CO}_2$ reforming system are considered as follows: methane cracking, $\text{CH}_4\text{--CO}_2$ reforming and CO_2 gasification. The three kinds

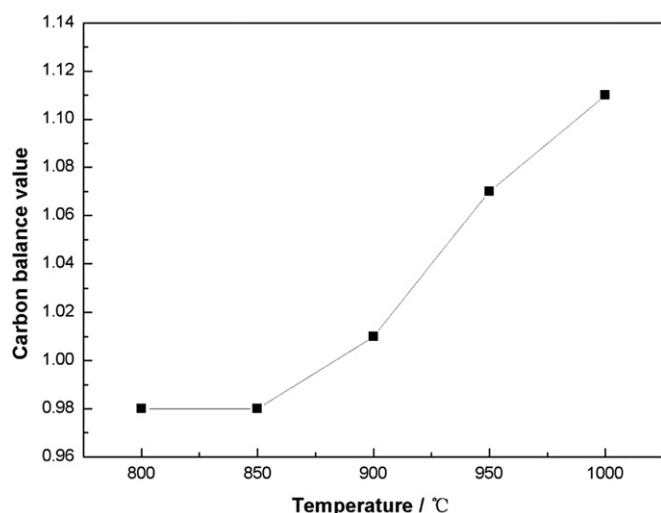


Fig. 5. Carbon balance value versus temperature.

of reactions are strongly endothermic reaction, so increasing the reaction temperature had a positive effect. The reports showed [20,21] that carbon may be formed via methane cracking and consumed via CO_2 gasification. Carbon dioxide reacts with the carbon (high activity) of methane cracking, and then reacts with the carbon of the semi-coke catalyst. The rate of CO_2 gasification is greater than that of methane cracking, which will result in the carbon consumption of semi-coke catalyst.

4. Changes in the surface properties of the semi-cokes before and after reaction

4.1. BET, volume and pore diameter

Table 2 shows the BET, volume and pore diameter of the semi-cokes before and after reaction. Table 2 shows that before the reaction, the BET for the Hongce lignite semi-cokes and Shenmu bituminous coal semi-cokes were almost the same, $47.8 \text{ m}^2 \text{ g}^{-1}$ and $39.3 \text{ m}^2 \text{ g}^{-1}$, respectively, and the BET for the Jincheng anthracite semi-cokes was smaller, $5.6 \text{ m}^2 \text{ g}^{-1}$. Their BET was related to their coal rank order, where the semi-cokes with lower coal ranks had more surfaces and pores, which is favourable for the adsorption of CH_4 and CO_2 . In 480 min, although the surface area was low, it indicated that the semi-cokes still had relatively stable catalytic activity. During the reforming reaction, there was gasification between CO_2 and the deposited carbon, eliminating some of the carbon deposition. In addition, the oxygen groups on the surface of semi-cokes actively react with the deposited carbon, lowering the effects of carbon deposition on the performance of the catalyst.

Table 2
BET, volume and average pore diameter of semi-cokes.

Sample	Micropore area ($\text{m}^2 \text{ g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{ g}^{-1}$)	Average pore diameter (nm)
HC before reaction	47.8	0.021	2.976
SM before reaction	39.3	0.018	3.421
JC before reaction	5.6	0.007	5.376
HC after reaction	42.4	0.018	3.137
SM after reaction	31.0	0.015	4.25
JC after reaction	3.9	0.006	7.743

4.2. FTIR analysis

Fig. 6 shows the FTIR of the three semi-cokes before and after the reaction. Fig. 6 shows that for all three semi-cokes, absorption peaks can be found near 3444 cm^{-1} , 1598 cm^{-1} , 1450 cm^{-1} , 1087 cm^{-1} , 1023 cm^{-1} and 797 cm^{-1} . The absorption peak at 3444 cm^{-1} is caused by the stretching and vibration of hydroxyl, OH, the absorption peak at 1598 cm^{-1} is caused by the stretching and vibration of carboxyl, $\text{C}=\text{O}$, the absorption peak at 1450 cm^{-1} is caused by the stretching and cutting vibration of nitrogen functional groups such as $-\text{NH}_2$, etc., the absorption peak at 1023 cm^{-1} is caused by the stretching and vibration of organic functional groups such as fat clusters and alkylene oxides, etc., and the absorption peak at 797 cm^{-1} is caused by the deformation vibration of $\text{C}-\text{H}$. From Fig. 6, we can see that the intensity of the absorption peak for the Hongce lignite semi-cokes was larger than those for the other semi-cokes, which indicates that the amount of functional groups on its surface was also higher. The hydroxyl OH peak and carboxyl $\text{C}=\text{O}$ peak of Hongce lignite semi-coke were all very strong.

After the reaction, the absorption peak near 1450 cm^{-1} almost vanished for all three semi-cokes, the absorption peak at 1023 cm^{-1} was obviously diminished for the Shenmu bituminous coal semi-cokes and Jincheng anthracite semi-cokes, and the absorption peak at 1598 cm^{-1} for the carboxyl $\text{C}=\text{O}$ function group almost disappeared. These changes indicate that the functional groups on the surface of the semi-cokes participated in the reforming reaction. However, after the reaction of the Hongce lignite semi-coke, the other absorption peaks did not become significantly weaker, which shows that the oxygen content in the Hongce lignite semi-coke is high, indicating that the oxygen functional groups result in the better catalytic performance of Hongce lignite semi-cokes.

4.3. XRD analysis

Fig. 7 shows the X-ray diffraction patterns for the three types of semi-cokes before and after the reaction. In this spectrum, 26.8° is the diffraction peak of graphite.

From Fig. 7(a), it can be observed that there are abundant mineral diffraction peaks, which exist in the three semi-cokes before the reaction. The minerals present in the Hongce semi-cokes are mainly the crystal forms of CaPO_4 , $\text{Mg}_{15}\text{V}_6\text{Mo}_5\text{O}_{48}$ and $\text{Na}_3\text{Sb}_5\text{F}_{18}$, in the Shenmu semi-cokes, the minerals are the crystal forms of CuV_2O_6 and $\text{CuFe}_2(\text{PO}_4)_2(\text{OH})_2$, in the Jincheng semi-cokes, the minerals are the crystal form of $\text{Al}_4\text{Si}_2\text{O}_9(\text{OH})_3$, and the K, Na, Mg, etc., alkaline metallic compounds function as catalysts. From Fig. 7(b), after 480 min of reaction, the diffraction peaks of the semi-cokes mainly show carbon and silica. The peaks for the alkaline earth metals have almost completely diminished because the high temperature of the reaction promoted the volatilisation of the Na, Mg, etc., metal ions, lowering the active material on the surface of the semi-cokes. This is also one of the reasons why the catalytic activity of the semi-cokes is lower.

4.4. SEM images of the semi-cokes

Fig. 8 shows the SEM images before the reaction and after 480 min of reaction. It can be observed that the surface topography of the three types of semi-cokes are quite different: the folding on the surface of the Hongce lignite semi-cokes is obvious, showing the layered structure, the surface of the Shenmu bituminous coal semi-cokes is a pore-distributed structure, the surface of the Jincheng anthracite semi-cokes is flat and compact with no obvious pore-distributed structure and with the edge clear of the

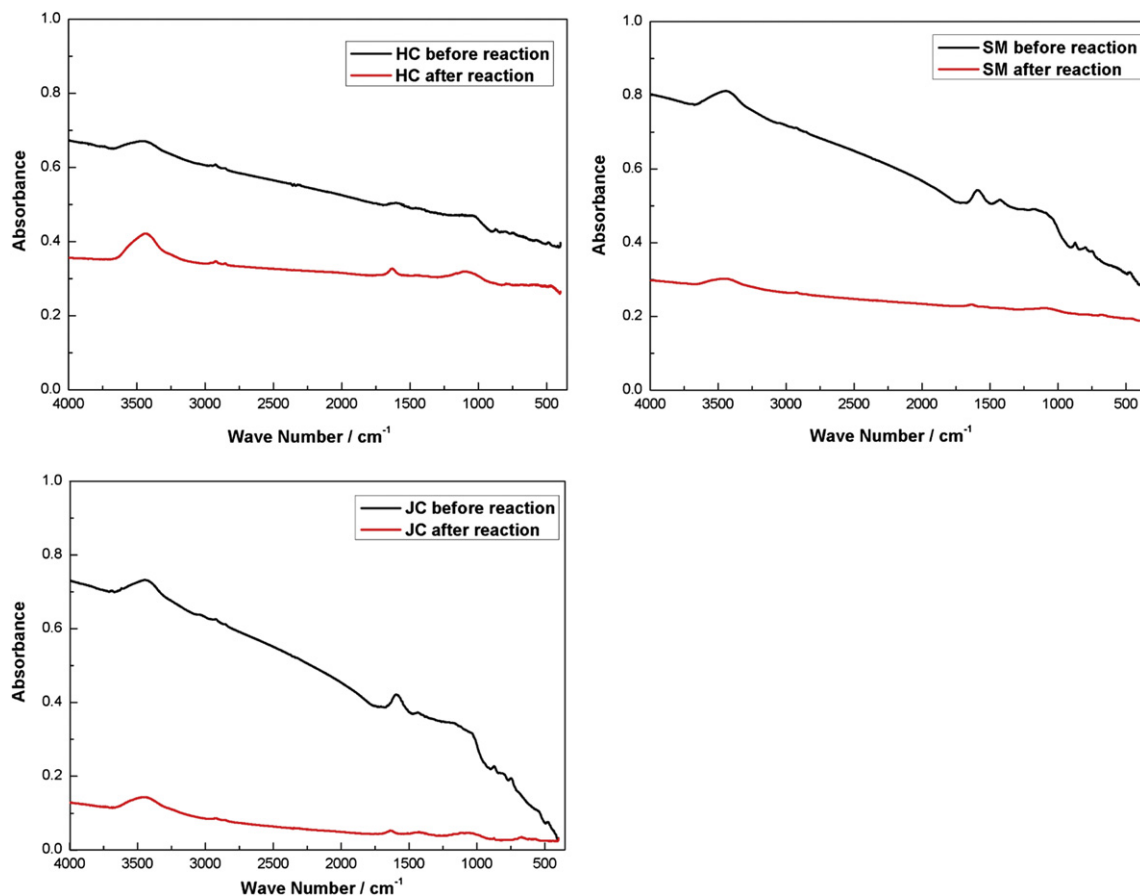


Fig. 6. FTIR of semi-coke.

particulates that are distributed on the surface. By comparing the 10 μm scale plate on the images, the surface of Hongce lignite semi-cokes is dominated by micropores, although there are obvious middle-sized pores and larger pores.

After the reaction, most of the folding structures of the Hongce lignite semi-coke disappeared, and many sinks were generated, resulting in the concave and convex structure. Additionally, many pores that were originally closed were opened and stretched inward. The original pore structure of the Shenmu bituminous coal

semi-cokes partially disappeared. However, the surface of the Jincheng anthracite semi-cokes was still somewhat flat and smooth, and the edge that was clear of the deposited particulates that were on the surface of the semi-cokes became round and smooth as the large deposited particulates were replaced by many micro-particulates. These changes indicate that the semi-cokes have participated in the reforming reaction, and, at the same time, they further explain why the higher activities were retained in the semi-cokes after the 480 min reaction.

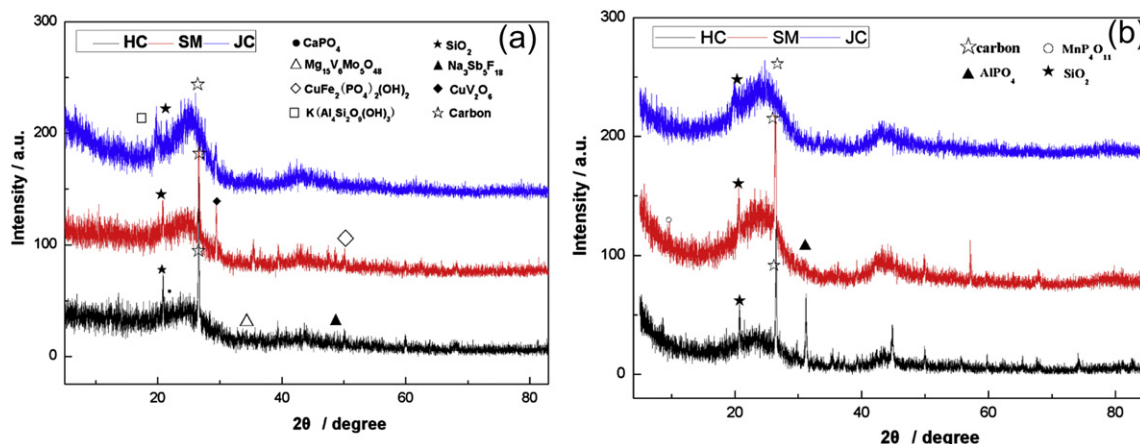


Fig. 7. XRD patterns of semi-cokes before (a) and after (b) reaction.

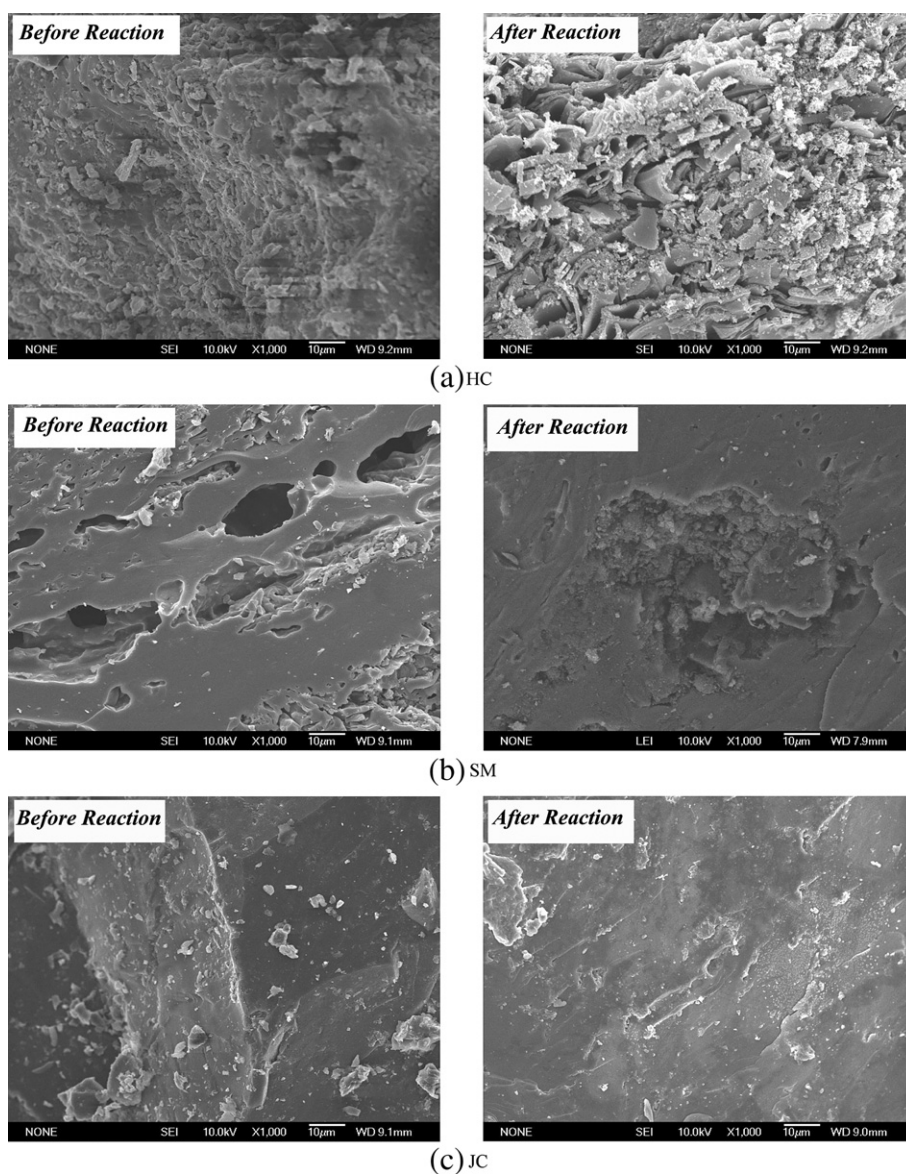


Fig. 8. SEM images of semi-cokes.

5. Conclusions

In a fixed-bed reactor, $\text{CH}_4\text{--CO}_2$ reforming has been studied over different semi-cokes. The $\text{CH}_4\text{--CO}_2$ reforming shows the same conversion trend with different semi-cokes, where the CH_4 and CO_2 conversions are higher at the initial phase, and as the reaction progresses, the conversions gradually decrease and tend to be stable. The results show that the catalytic activity varies for the different types of semi-cokes, and the catalytic activity of the Hongce lignite semi-cokes is much better than that of the Shenmu bituminous coal semi-cokes and the Jincheng anthracite semi-cokes under the same conditions. By analysing the surface structure of the semi-cokes before and after the reaction, it is shown that the C=O and --NH_2 , etc., functional groups all participated in the reforming reaction. The ultimate and infrared analysis shows that the oxygen content in the Hongce lignite semi-cokes is the highest, and the content of the corresponding functional group is large, resulting in better catalytic activity. The lower rank of the coal rank results in the better catalytic activity of the semi-cokes.

Acknowledgements

The authors are grateful to the National Basic Research Program of China (2012CB723105), the National Science & Technology Pillar Program of China (2012BAA04803) and the National Natural Science Foundation of China (51274147, 21006066) for financial support of the present study.

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